Thermochimica Acta 501 (2010) 98–102

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

A DSC investigation on the changes in pore structure of skin during leather processing

N. Nishad Fathima, M. Pradeep Kumar, J. Raghava Rao*, B.U. Nair

Chemical Lab, Central Leather Research Institute, Council of Scientific and Industrial Research, Adyar, Chennai 20, India

ARTICLE INFO

Article history:
Received 7 September 2009
Received in revised form 2 December 2009
Accepted 12 January 2010
Available online 18 January 2010

Keywords:
Pore structure
Thermoporometry
Differential scanning calorimetry (DSC)
Skin
Leather
Scanning electron microscopy (SEM)

ABSTRACT

Leather processing involves many unit operations that modify the physical, chemical and biological properties of the raw skin/hide of an animal. One such major variation is brought to pore structure and size, which determines the breathing property of skin. Understanding this property is essential to improve the end use of the leather matrix. Thermoporometric technique has been used in this study to bring out the influence of various process steps on the pore size distribution of skin. Marked changes in the depression of freezing point are observed for each process. Scanning electron microscopy study reveals the morphological changes in the grain and cross-section of the skin during leather processing. Understanding and predictions of pore structure changes at various stages of leather processing would benefit: (a) in process control, (b) analysis of cost benefit ratio and (c) strategic planning and transport. Thus, this study aids in better understanding of the pore structure of skin to improve the functional properties of the leather.

1. Introduction

Properties such as shape, volume, and size distribution influence functional behavior of porous media. Hence, understanding the effect of various process parameters on the pore structure of a material will help in enhancing its functional properties. Leather is a three-dimensional matrix with its excellent pore connectivity. Leather is a unique material with ability to breathe and readjusts itself to volume fluctuations of foot. This present study aims at understanding the influence of process steps involved in leather making on the pore structure of skin. Thermoporometry is a technique that allows the study of pore structures of materials in the liquid state. This method of determining the pore size distribution in materials suggested by Kuhn et al. [1] and later derived by Brun et al. [2], uses a thermodynamical relationship based on Gibbs–Thomson equation. The phase transitions at triple point (crystallization or melting) for a liquid confined within a pore are known to be shifted to lower temperatures depending on the distribution of pore size. This difference in transition temperature, ΔT, between confined and bulk solvent can be detected calorimetrically by differential scanning calorimetry (DSC).

From the DSC experiments, water absorbed in hydrophilic materials is categorized as non-freezing bound-, freezing bound-, and unbound water [3–5]. Water adjacent to a surface and forming a part of three layers may not freeze at the temperatures or local bulk water could freeze. This is because the motion of water structures could be limited in confined media due to interaction with surfaces [6]. Freezing bound water has thermodynamically different behavior compared to unbound water. The quantity of freezing bound water could be determined by the integration of either an exotherm (crystallization of water) or an endotherm (melting of water) [4,7–9]. However, freezing bound water is generally characterized by the integration of the endotherm [10,11]. Melting temperature of water held in capillaries of porous materials is known to be lowered on depression. Since the depression of melting temperature bears a reciprocal relationship with the pore diameter, distribution of pore size in materials can be estimated using thermoporometric principles.

Several techniques like mercury intrusion porosimetry, nitrogen adsorption, scanning electron microscopy, and atomic force microscopy have been successfully employed for the analysis of pores of various materials [12,13]. These techniques are suitable only for dry samples. Thermoporometry has been used in this study to analyze the changes in the pore size distribution of skin at each step of leather processing as it enables the measurement of pore structure in wet condition. Leather processing involves many unit operations [14]. The skin matrix goes through changes in the pH as well as the pore structure during these processes. Changes brought about in the pore structure of skin matrix when subjected to heat viz. on shrinkage and the effect of tanning agents on this phenomenon have been studied [15–17]. In this study, the variation

* Corresponding author. Tel.: +91 44 2441 1630; fax: +91 44 2491 1589.
E-mail address: clrichem@mailcity.com (J.R. Rao).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.01.016

in the pore size distribution of skin during various stages of leather processing has been addressed. This study will throw light on how the microscopic changes in pore structure affect the dimensional changes and properties of the material.

2. Materials and methods

2.1. Materials and preparation of sample

Goat skin was taken as the raw material. Soaking, liming, deliming, pickling and chrome tanning were carried out as per standard procedures [18].

2.2. Differential scanning calorimetry (DSC) measurements

The samples at various stages of leather processing (3–5 mg by weight) were blotted uniformly to remove excess adhering water and hermetically encapsulated in aluminium pans. The samples were fused in a differential scanning calorimetric cell of a DSC Q 200 TA instruments differential scanning calorimeter. The temperature was calibrated effectively using indium as standard. Prior to measurement, the vessel was cooled to −40 °C and held at that temperature for 30 min. The heating rate was maintained as 1 °C/min. All measurements were carried out between −40 and 10 °C. At the end of each measurement, the vessel was dried under vacuum for 24 h to attain the mass of dry fibers. The moisture content was maintained at about 65–68% for all samples. All measurements were carried out in triplicates and average values are reported. Pore size distribution was determined by measuring the amount of water that has its melting temperature depressed at each step. The enthalpies (S_1, S_2, S_3 . . ., S_i J/g) obtained from the DSC is noted to the corresponding temperatures (T_1, T_2, T_3, . . ., T_i °C) with step size 0.1 K and the pore radius is calculated as per Eq. (1).

$$R_p = -\left(\frac{32.33}{T - T_0}\right) + 0.68 \quad (1)$$

where T and T_0 are the melting temperatures of sample and solvent, respectively. From the obtained radii, the average temperature interval T_i' is calculated for corresponding pore radius R_p as per Eq. (2).

$$T_i' = \frac{T_i + T_{i+1}}{2} \quad (2)$$

The volumic latent heat W_v (J/cm^3) is derived by the ratio of specific latent heat of fusion W_s (J/g) to specific volume of solvent V (cm^3/g) as per Eq. (3).

$$W_v = \frac{W_s}{V} \quad (3)$$

where $W_s = -(0.0556(T_i' - T_0)^2 - 11.39(T_i' - T_0) - 332)$ and $V = 1.000132(1 - 0.000091T_i' + (1.035 \times 10^{-5})T_i'^2)$.

The pore volume ΔV (cm^3/g) is further derived from the enthalpy and volumic latent heat as per Eq. (4).

$$\Delta V = \frac{S_i}{W_v \times M \times 1000} \quad (4)$$

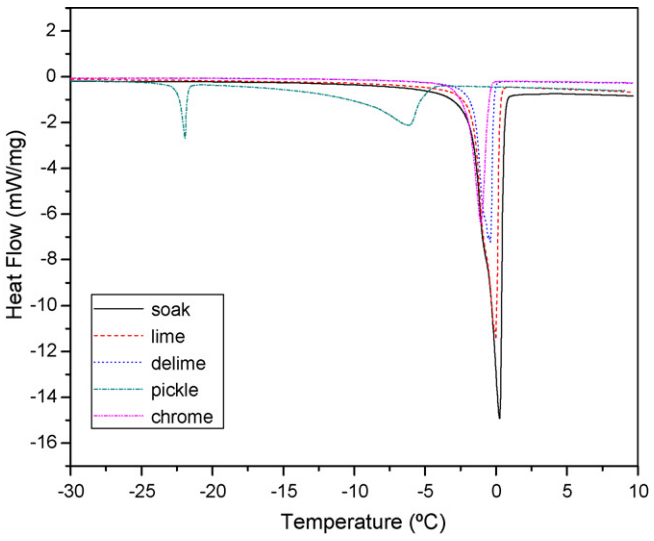

Fig. 1. Heat flow versus temperature thermograms of (a) soak; (b) limed; (c) delimed; (d) pickled; (e) chrome tanned at scan rate 1 °C/min.

where M = mass of dry sample in grams. The pore volume and the corresponding average temperature interval are substituted in Eq. (5) to obtain pore volume distribution (cm^3/g nm) and graph is plotted for pore volume distribution versus pore radius to compare the changes in pore structure in course of leather processing.

$$\frac{dV}{dR_p} = \frac{\Delta V}{T_i - T_{i+1}} \quad (5)$$

2.3. Scanning electron microscopy (SEM) measurements

Samples were cut at various stages of leather processing. Samples were prepared for the SEM analysis by gradual dehydration with acetone such that the pores were not altered [19]. SEM micrographs were taken using Hitachi scanning electron microscope at 15 kV at various magnifications. Ion sputter coater with gold target was used for coating the samples.

3. Results and discussion

Structure and connectivity of pores in skin influence the heat and mass transport processes associated with the thermoregulatory function of the organ. Leather derives its unique property of breathability through this porous network. The conversion of skin into leather subjects the matrix to various physical and chemical operations. The effect of these process conditions on the pore structure of leather has been studied using thermoporometry. The differential scanning calorimetric investigations have been made on skin after every stage of leather processing, viz., soaking, liming, deliming, pickling and tanning (Fig. 1a–e). The melting peak of the thermogram occurred at −0.57 °C for the soaked skin whereas liming and other operations led to significant depression of melting temperature as presented in Table 1. The enthalpy of phase transi-

Table 1
Thermodynamic parameters from DSC thermograms of skin at various stages of leather processing.

Sample	Onset (°C)	Peak (°C)	Enthalpy (J/g)
Soaked	−1.21 ± 0.02	−0.57 ± 0.01	163.1 ± 0.5
Limed	−1.24 ±0.01	−0.64 ± 0.02	177.6 ± 0.7
Delimed	−1.21 ± 0.01	−0.75 ± 0.02	147.8 ± 0.4
Pickled	−22.38 ± 0.02, −10.46 ± 0.02	−22.07 ± 0.02, −6.21 ± 0.01	13.50 ± 0.2, 84.81 ± 0.3
Chrome tanned	−2.08 ± 0.01	−1.05 ± 0.01	184.2 ± 0.7

tion of water in the skin is also presented in Table 1. The capillary structure of collagen fibers seems to be influenced by the nature of the interaction with the various chemicals used in each process. This is inferred from both depression of melting and enthalpy changes associated with water constrained in the skin.

The thermoporometric investigations on skin reveal dramatic variations in pore size distributions in each stage of leather processing as seen from the data presented in Fig. 2. Soaking is an operation where the skin is washed with water to remove the adhering dirt and it is in the native condition. In soaked skin, pore size distri-

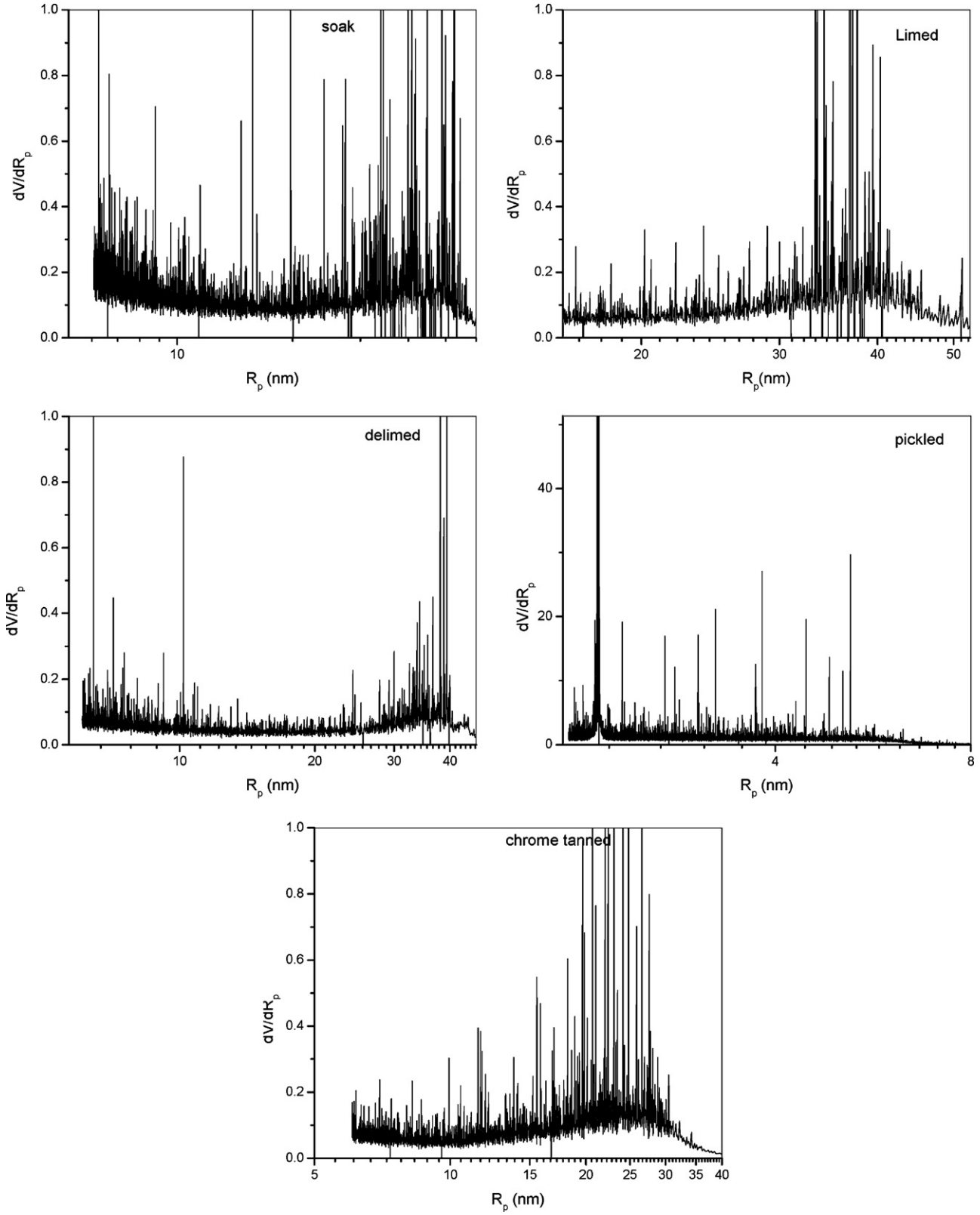

Fig. 2. Pore size distribution of samples at various stages of leather processing (pore volume distribution dV/dR_p, $cm^3/g\,nm$ versus pore radius R_p, nm).

bution varied in the range of 5–55 nm. Liming operation involves addition of chemicals like lime and sulfide to open up the fiber structure for easy removal of hair and flesh from the skin. This leads to a swollen matrix. This change in the structure can be seen from Fig. 2, which shows that liming shifts the pore size distribution to larger sizes in the 30–40 nm range. Deliming operation involves the removal of lime added during the previous operation. It is evident from the figure, that restoration of the matrix structure to the original condition, viz., de-swelled condition is achieved. Pickling operation involves the addition of acid and salt to the matrix to prepare it for the tanning operation. There are two transitions seen for the pickled skin (Fig. 1d) one for the freezing of pore water at −6.1 °C and salt-water eutectic temperature at −21.9 °C [20] unlike other process samples and this is due to the use of salt during pickling operation. It can be seen from Fig. 2 that this leads to drastic changes in the pore structure of skin, the pore size is limited to 1–6 nm as against the 30–40 nm pore size distribution for other samples.

In order to visualize the effect of various leather processing steps on the pore structure of skin, scanning electron microscopy studies were carried out. Scanning electron micrographs showing the grain and cross-section of samples taken at various stages of leather processing are given in Figs. 3 and 4, respectively. It is seen from Fig. 3, that the grain surface reflects clearly the effect of each process step. Fig. 3a shows the grain surface of the soaked sample where the presence of hair is seen. Fig. 3b, which is the grain surface of the limed sample shows the pores without any hair as liming operation results in complete removal of hair from the roots. Grain surface of deliming and bating samples Fig. 3c,d show that there is not much influence of these operations on the grain surface of the skin. The SEM micrograph of pickled sample (Fig. 3e) shows clearly the deposition of salt on the grain surface as it is used during this process to prevent swelling due to use of acid. The chrome tanned sample shows clear surface where there are no depositions of any chemicals. Fig. 4a gives the cross-section of soaked sample and it can be seen that the fibers are compacted and dense. The cross-section of the limed sample (Fig. 4b) shows that the fibers are split as liming results in fiber opening. The subsequent operation, deliming results in de-swelling hence the fibers are brought back to the native state. The cross-section of bated sam-

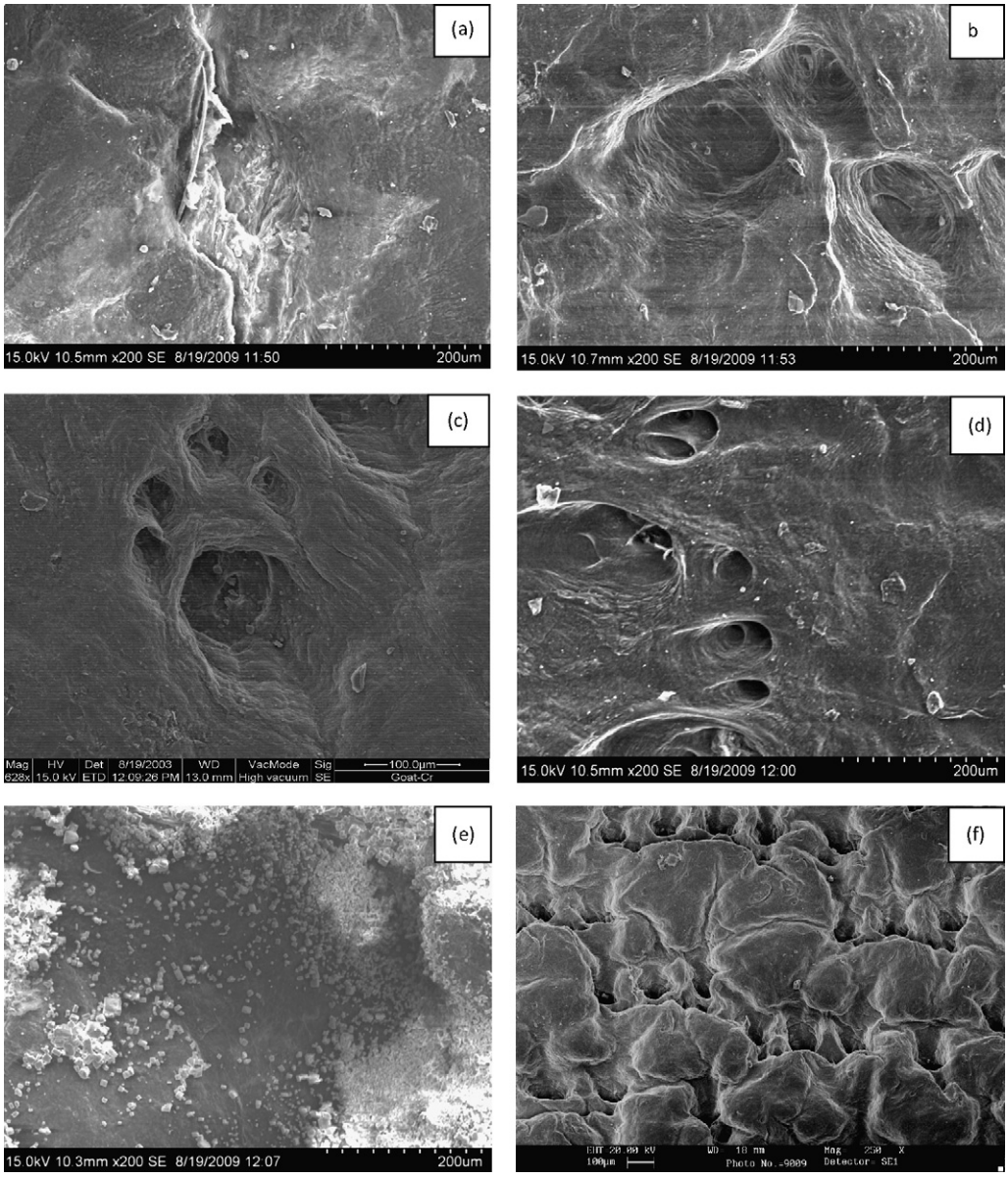

Fig. 3. Scanning electron micrograph showing the grain surface (200×) of (a) soak; (b) limed; (c) delimed; (d) bated; (e) pickled; (f) chrome tanned leather.

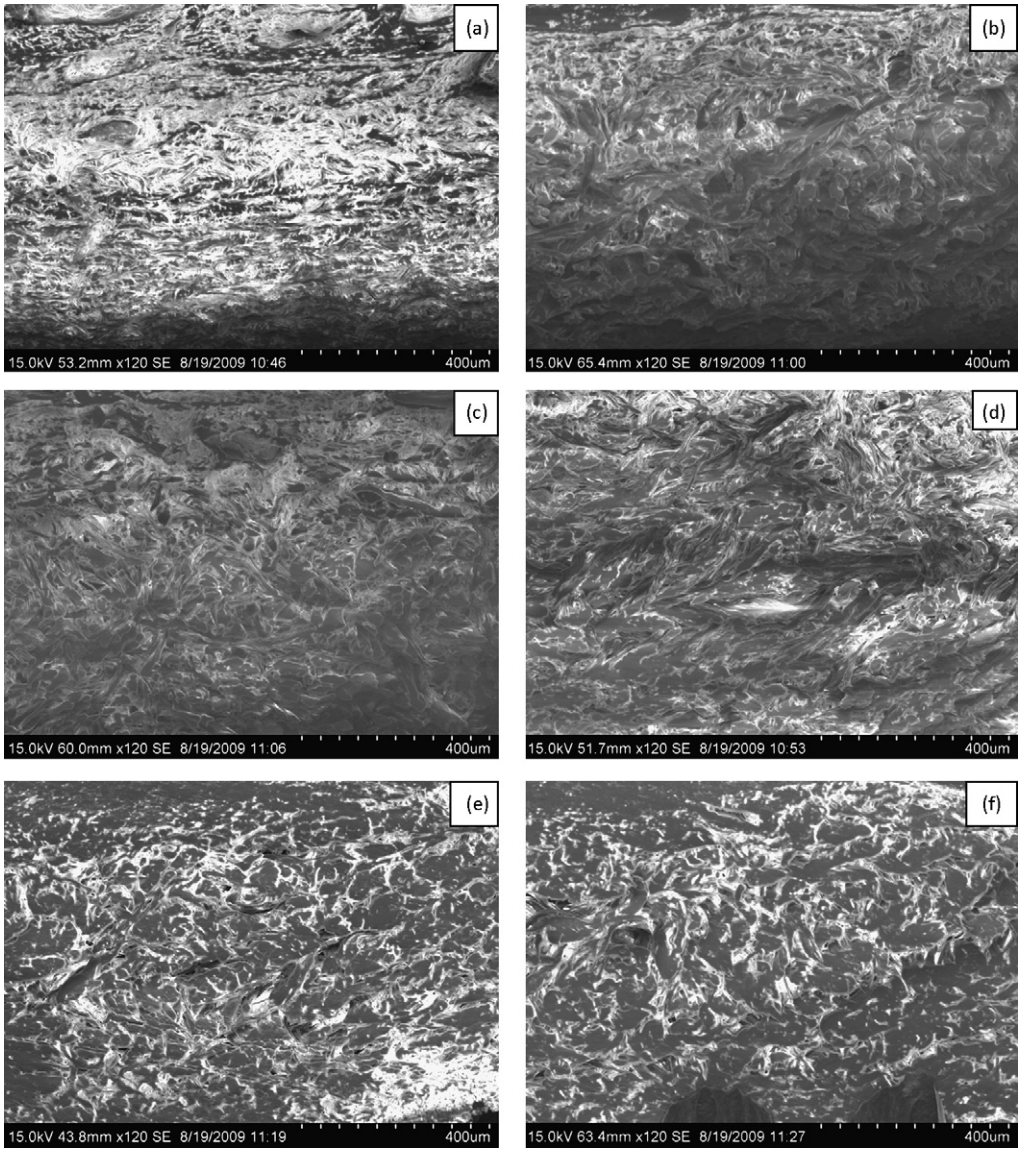

Fig. 4. Scanning electron micrograph showing the cross-section (120×) of (a) soak; (b) limed; (c) delimed; (d) bated; (e) pickled; (f) chrome tanned leather.

ple (Fig. 4e) shows fibers which are well dispersed as enzymes used during this operation result in removal of other fibrous proteins like elastin and reticulin. As chrome tanning is a non-filling type of tanning process, the fiber structure (Fig. 4f) does not show much compaction.

4. Conclusions

The present study demonstrates the various changes, which the skin undergoes during leather making. The porosity of skin is an important parameter, which enables the leather to breathe. Hence, monitoring the changes happening to the skin during leather processing would help in maximizing this property in the final leather by making appropriate changes in the process.

References

[1] W. Kuhn, E. Peterli, H. Majer, J. Polym. Sci. 16 (1955) 539–548.
[2] M. Brun, A. Lallemand, J.F. Quinson, C. Eyraud, Thermochim. Acta 21 (1977) 59–88.
[3] W.G. Liu, K.D. Yao, Polymer 42 (2001) 3943–3947.
[4] K. Nakamura, T. Hatakeyama, H. Hatakeyama, Textile Res. J. 51 (1981) 607–613.
[5] Z.H. Ping, Q.T. Nguyen, S.M. Chen, J.Q. Zhou, Y.D. Ding, Polymer 42 (2001) 8461–8467.
[6] E. Berlin, P.G. Kliman, M.J. Pallansch, J. Colloid Interface Sci. 34 (1970) 488–494.
[7] H. Sakabe, H. Ito, T. Miyamoto, H. Inagaki, Textile Res. J. 57 (1987) 66–72.
[8] T. Yamamoto, S.R. Mukai, K. Nitta, H. Tamon, A. Endo, T. Ohmori, M. Nakaiwa, Thermochim. Acta 439 (2005) 74–79.
[9] M.R. Landry, Thermochim. Acta 433 (1–2) (2005) 27–50.
[10] T. Hori, H.S. Zhang, T. Shimizu, Textile Res. J. 58 (1988) 227–232.
[11] T. Yamauchi, K. Murakami, J. Pulp Paper Sci. 17 (1991) 223–226.
[12] J.R. Kanagy, J. Am. Leather Chem. Assoc. 58 (1963) 524–550.
[13] A.C. Zettlemoyer, E.D. Schweitzer, W.C. Walker, J. Am. Leather Chem. Assoc. 41 (1946) 253–264.
[14] N.N. Fathima, S. Saravanabhavan, J.R. Rao, B.U. Nair, J. Am. Leather Chem. Assoc. 99 (2004) 73–81.
[15] N.N. Fathima, A. Dhathathreyan, T. Ramasami, J. Am. Leather Chem. Assoc. 96 (2001) 417–425.
[16] N.N. Fathima, A. Dhathathreyan, T. Ramasami, Biomacromolecules 3 (2002) 899–904.
[17] N.N. Fathima, A. Dhathathreyan, T. Ramasami, Colloids Surf. B: Biointerfaces 57 (2007) 118–123.
[18] T.C. Thorstensen, Practical Leather Technology, 2nd ed., Krieger, Huntington, 1976.
[19] P. Echlin, in: V.H. Heywood (Ed.), Scanning Electron Microscopy, vol. 4, Academic Press, London, 1971, p. 307.
[20] P. Kamasa, M. Bokor, M. Pyda, K. Tompa, Thermochim. Acta 464 (2007) 29–34.